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THIXOTROPIC REACTIVE COMPOSITION

Technical Field

The present invention pertains to the field of the thixotroping of reactive
10 compositions, especially of adhesives and sealants.

Prior Art

For the application of an adhesive or sealant the thixotropy is an
important feature. Adhesives and sealants are typically stored in cartridges,
15 pails or drums. For application they are withdrawn from this storage vessel by
pumps, or by expressing using a cartridge gun or follower plates, and are
applied to the substrate to be bonded or sealed, typically by means of a nozzle,
where appropriate by a static mixer. To maximize conveying efficiency and
minimize force expenditure it is advantageous for the adhesive or sealant to
20 have a very low viscosity. On the other hand, the applied adhesive or sealant
ought to remain in the applied shape and not run off after application. This is
enormously important particularly in the case of thick layers or in the case of
vertical or overhead applications. For maximizing shape retention a very high
viscosity is of advantage.

25 These requirements of conveying and shape preservation are
completely contradictory. The skilled worker is aware, however, of the
phenomenon of thixotropy. With this effect a material becomes less viscous as
soon as it is agitated, and solidifies again when the agitation ceases again.
This effect is therefore utilized by the majority of commercial adhesives and
30 sealants. The adhesive, or the moderately viscous binder, is typically admixed
with an additive. Examples of such thixotropic agents are inorganic substances

such as, for example, bentonites or pyrogenic silicas, or organic substances such as castor oil derivatives, specific polyamides or polyureas.

Thus, for example, DE 23 60 019 describes a polyurea thixotropic agent which results from the reaction of primary and/or secondary polyamines,
5 monofunctional alcohols and/or amines with diisocyanate compounds.

A thixotropic agent for polyurethane compositions based on a urea derivative in a nondiffusing carrier material is described in EP 1 152 019 A1, for example.

(Meth)acrylates having a functionality of more than two are used
10 primarily for fast-crosslinking and extremely resistant coating materials. US 3,663,467 describes a porous polymer based on trimethylolpropane trimethacrylate which is used for absorbing phenol from hexane. EP 0 732 348 A1 describes a moisture-curing polymer composition containing fine particles of a copolymer of a mono(meth)acrylate with a monomer having
15 two or more (meth)acryloyloxy groups, the fraction of the latter being not more than 10 mol% of the copolymer and being said to lead to increased extension and impact strength.

Exposition of the Invention

20 The object was to find a new form of thixotroping reactive compositions. Surprisingly it was found that this can be achieved by a thixotropic composition as claimed. In particular it was found that the compound **B** is suitable as a thixotropic agent for broad-spectrum use in reactive compositions.

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Embodiments of the Invention

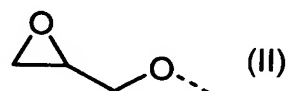
The present invention relates to a thixotropic composition which comprises at least one compound **A** having at least two reactive groups which are selected from the group comprising isocyanate, epoxide, alkoxysilane, and
30 mixtures thereof, and also at least one polymeric thixotropic agent **B** prepared by homopolymerizing a (meth)acrylate **B1** or by copolymerizing a (meth)acrylate **B1** with at least one further (meth)acrylate. The (meth)acrylate

mixture here possesses an average (meth)acrylate functionality \bar{f} of 2.5 to 4.5.

By "(meth)acrylate" is meant throughout the present documents an ester of acrylic acid or methacrylic acid, the term therefore encompassing both
5 methacrylates and acrylates.

By "alkoxysilane" is meant throughout the present document an organosilicon compound in which at least one organic radical is bound via a C-Si bond to the silicon atom and which possesses at least one further organic radical which is bound via an O-Si bond to the silicon atom radical.

10 By "epoxy" is meant throughout the present document the one oxirane group, formula (I), of which the glycidyl group, formula (II), represents the preferred variant.



By "poly" in "polyol", "polyamine", "polymercaptane" and "polyisocyanate" is meant in the present document molecules which formally
15 contain two or more of the respective functional groups.

The term "polyurethane" encompasses in the present document all polymers which are prepared by the diisocyanate polyaddition process. This includes even those polymers which are virtually or entirely free from urethane groups, such as polyether-polyurethanes, polyester-polyurethanes, polyether-
20 polyureas, polyureas, polyester-polyureas, polyisocyanurates, polycarbodiimides, etc.

By "(meth)acrylate functionality" is meant the number of (meth)acrylate groups per molecule, and, accordingly, reference is made to "monofunctional", "difunctional", "trifunctional", "tetrafunctional", and "pentafunctional"
25 (meth)acrylates.

The "average (meth)acrylate functionality \bar{f} " is calculated according to the following formula:

$$\bar{f} = \frac{\sum_i n_i f_i}{\sum_i n_i}$$

In this formula n_i is the number of moles of the respective (meth)acrylate in the (meth)acrylate mixture and f_i is its (meth)acrylate functionality. In order to prevent any absences of clarity it is mentioned additionally that \bar{f} is determined taking into account only substances which have at least one (meth)acrylate function; in other words, any other substances that may be present in this mixture during the copolymerization, such as solvents, plasticizers, compound **A** or the reactants of **A**, for example, are not taken into account.

The composition of the invention comprises at least one compound **A**. This compound **A** possesses at least two reactive groups. These reactive groups are isocyanate, epoxide or alkoxysilane groups. The compound **A** may also contain mixtures of these groups. Thus, for example, the compound **A** may contain simultaneously alkoxysilane and isocyanate groups or simultaneously alkoxysilane and epoxy groups or epoxy and isocyanate groups. It is even possible for the compound **A** to contain simultaneously alkoxysilane, epoxy and isocyanate groups. It is preferred, however, for the compound to contain at least two identical groups.

The compound **A** is in particular a polymer or oligomer.

In one embodiment the compound **A** is a compound **A3** which is a polyurethane prepolymer containing at least two isocyanate groups. This polyurethane prepolymer is preparable from at least one polyol and at least one polyisocyanate.

This reaction may take place by the polyol and the polyisocyanate being reacted by typical methods, such as at temperatures of 50°C to 100°C for example, with or without the use of suitable catalysts, the amount of polyisocyanate added being such that its isocyanate groups are present in a stoichiometric excess in relation to the hydroxyl groups of the polyol. The excess of polyisocyanate is chosen such that the residual free isocyanate group content of the resulting polyurethane prepolymer **A3**, after the reaction of all hydroxyl groups of the polyol, is 0.1% to 15% by weight, preferably 0.5% to

5% by weight, based on the total polyurethane prepolymer **A3**. Where appropriate, the polyurethane prepolymer **A3** can be prepared using plasticizers, the plasticizers used containing no isocyanate-reactive groups.

- 5 As polyols for preparing the polyurethane prepolymer **A3** it is possible for example to use the following commercially customary polyols or any desired mixtures of them:

-Polyoxyalkylene polyols, also called polyether polyols, which are
10 polymerization products of ethylene oxide, 1,2-propylene oxide, 1,2- or 2,3-butylene oxide, tetrahydrofuran or mixtures thereof, optionally polymerized by means of a starter molecular having two or more active hydrogen atoms, such as, for example, water, ammonia or compounds having two or more OH or NH groups, such as, for example, 1,2-ethanediol, 1,2- and 1,3-propanediol,
15 neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol, bisphenol A, hydrogenated bisphenol A, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane,
20 glycerol, aniline, and mixtures of the aforementioned compounds. It is possible to use polyoxyalkylene polyols which have a low degree of unsaturation (measured according to ASTM D-2849-69 and expressed in milliequivalents of unsaturation per gram of polyol (meq/g)), prepared for example by means of what are called double metal cyanide complex catalysts (DMC catalysts), but
25 also polyoxyalkylenepolyols having a higher degree of unsaturation, prepared for example by means of anionic catalysts such as NaOH, KOH or alkali metal alkoxides.

Particular suitability is possessed by polyoxyalkylene diols or polyoxyalkylene triols, especially polyoxypropylene diols or polyoxypropylene triols.

- 30 Especially suitable are polyoxyalkylene diols or polyoxyalkylene triols having a degree of unsaturation of less than 0.02 meq/g and having a molecular weight in the range from 1000 to 30 000 g/mol, and also

polyoxypropylene diols and triols having a molecular weight of 400 to 8000 g/mol. "Molecular weight" or "molar weight" in the present document always refers to the molecular weight average M_n .

Likewise particularly suitable are what are called "EO-endcapped" (ethylene oxide-endcapped) polyoxypropylene diols or triols. The latter are special polyoxypropylene-polyoxyethylene polyols which are obtained, for example, by alkoxyating straight polyoxypropylene polyols, after the end of the polypropoxylation, with ethylene oxide, and which as a result contain primary hydroxyl groups.

-Hydroxy-functional polybutadienes.

-Polyester polyols, prepared for example from dihydric to trihydric alcohols such as, for example, 1,2-ethanediol, diethylene glycol, 1,2-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, glycerol, 1,1,1-trimethylolpropane or mixtures of the aforementioned alcohols, with organic dicarboxylic acids or their anhydrides or esters, such as, for example, succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydrophthalic acid, or mixtures of the aforementioned acids, and also polyester polyols of lactones such as ϵ -caprolactone, for example.

-Polycarbonate polyols of the kind obtainable by reacting, for example, the abovementioned alcohols – those used to synthesize the polyester polyols – with dialkyl carbonates, diaryl carbonates or phosgene,

-polyacrylate and polymethacrylate polyols.

These stated polyols have an average molecular weight of 250 to 30 000 g/mol and an average OH functionality in the range from 1.6 to 3.

Further to these stated polyols it is possible to use low molecular mass dihydric or polyhydric alcohols such as, for example, 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol,

hydrogenated bisphenol A, dimeric fatty alcohols, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, glycerol, pentaerythritol, sugar alcohols, and other polyhydric alcohols, low molecular mass alkoxylation products of the aforementioned dihydric and polyhydric alcohols, and mixtures of the
5 aforementioned alcohols when preparing the polyurethane prepolymer **A3**.

The polyurethane prepolymer **A3** is prepared using commercially customary polyisocyanates. Examples that may be mentioned include the following polyisocyanates, which are very well known in polyurethane
10 chemistry:

toluene 2,4- and 2,6-diisocyanate (TDI) and any desired mixtures of these isomers, diphenylmethane 4,4'-diisocyanate (MDI), the positionally isomeric diphenylmethane diisocyanates, phenylene 1,3- and 1,4-diisocyanate, 2,3,5,6-tetramethyl-1,4-diisocyanatobenzene, 1,6-hexamethylene diisocyanate
15 (HDI), 2-methylpentamethylene 1,5-diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene 1,6-diisocyanate (TMDI), dodecamethylene 1,12-diisocyanate, cyclohexane 1,3- and -1,4-diisocyanate and any desired mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (i.e., isophorone diisocyanate or IPDI), perhydrodiphenyl methane 2,4'- and
20 4,4'-diisocyanate (HMDI), 1,4-diisocyanato-2,2,6-trimethylcyclohexane (TMCDI), xylene m- and p-diisocyanate (XDI), tetramethylxylylene 1,3- and 1,4-diisocyanate (TMXDI), 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, and oligomers and polymers of the aforementioned isocyanates, and also any desired mixtures of the aforementioned isocyanates. Particular preference is
25 given to diisocyanates, especially MDI, TDI, HDI, and IPDI.

In a further embodiment the compound **A** is a compound **A1** which is a diglycidyl ether of bisphenol A, bisphenol F, bisphenol A/F, a mixture or an oligomer thereof. The designation 'A/F' refers in this context to a mixture of
30 acetone with formaldehyde, that is used as a reactant in its preparation. Among the diglycidyl ethers the compound is preferably a liquid resin. Owing to the preparation processes for these resins it is clear that constituents of higher

molecular mass are also present in the liquid resins. Liquid resins of this kind are available for example as Araldite® GY 250, Araldite® PY 304, Araldite® GY 282 (formerly Vantico, now Huntsman) or D.E.R.® 331 (Dow).

In addition it is possible for there to be further glycidyl ethers in the composition, known to the skilled worker as resins or reactive diluents. Particularly suitable reactive diluents are glycidyl ethers of alkyl radicals, alkylene radicals, and phenols, such as, for example, hexanediol diglycidyl ether, polypropylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, phenyl glycidyl ether or cresol glycidyl ether.

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In a further embodiment the compound A is a compound A2 which represents a polymer having at least two alkoxysilane groups. On the one hand the compound A2 represents a compound A2-1 and on the other hand it represents a compound A2-2.

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The compound A2-1 is a polyurethane prepolymer which contains at least two alkoxysilane groups. A2-2 can be prepared from a prepolymer containing isocyanate groups, corresponding to the identity and preparation of A3, and at least one compound which at least one alkoxy group and organic radical thereof, an NCO-reactive group, in particular a mercapto-alkoxysilane or an amino-alkoxysilane. In particular they are selected from the group comprising 3-aminopropyltrimethoxysilane, 3-aminopropyldimethoxymethylsilane, aminomethyltrimethoxysilane, aminomethyldimethoxymethylsilane, 3-amino-2-methylpropyltrimethoxysilane, 4-aminobutyltrimethoxysilane, 4-aminobutyldimethoxymethylsilane, 4-amino-3-methylbutyltrimethoxysilane, 4-amino-3,3-dimethylbutyltrimethoxysilane, 4-amino-3,3-dimethylbutyldimethoxymethylsilane, 2-aminoethyltrimethoxysilane, 2-aminoethyldimethoxymethylsilane, aminomethyltrimethoxysilane, aminomethyldimethoxymethylsilane, aminomethylmethoxydimethylsilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyldimethoxymethylsilane, 7-amino-4-oxaheptyldimethoxymethylsilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyldimethylmethoxysilane, and also their analogs with ethoxy or isopropoxy groups instead of the

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methoxy groups. In one embodiment the aminoalkoxysilane is an adduct of one of the aminoalkoxysilanes just specified with a maleic ester or fumaric ester, as described for example in US 5,364,955.

5 The compound **A2-2** is a polyether containing at least two alkoxy silane groups and are very well known to the skilled worker under the term of MS polymers and are described for example in US 6,207,766 in column 4 lines 27 to 54 and in US 3,971,751.

 The compounds **A2-2** can be prepared by a hydrosilylation reaction
10 from polyether containing at least two C=C double bonds, in particular from allyl-terminated polyoxyalkylene polymers, and from a compound $\text{HSi}(\text{R}^1)_a(\text{OR}^2)_{3-a}$. R^1 and R^2 here are independently of one another a C_1 - C_8 -alkyl radical, in particular methyl or ethyl, and a represents the value 0 or 1, in particular the value 0. For the hydrosilylation reaction a catalyst is used,
15 typically a platinum catalyst. One of the advantages of the compounds **A2-2** is that they can be prepared without the use of isocyanates and another is that these compounds have particularly low viscosity, and so are very suitable for use in one-component moisture-curing compositions.

20 For the compound **A2** it is preferred if the alkoxy silane groups are trimethoxy or triethoxy groups, especially trimethoxy groups.

 The compound **A** can also be obtained by reaction of a polyurethane prepolymer **A3** containing at least two isocyanate groups with at least one
25 compound **AX**. The compound **AX** contains an NCO-reactive group, especially primary or secondary amino group or SH group or OH group, and also one or more epoxide or alkoxy silane groups. The polyurethane prepolymers **A3** suitable for this purpose, and also their preparation, have already been described earlier in this specification. As compound **AX** it is possible for
30 example to use aminosilanes, mercaptosilanes or hydroxy-epoxides. In one particularly preferred embodiment the compound **AX** is a Michael adduct of

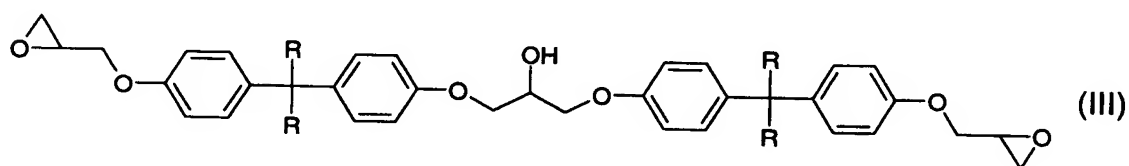
aminoalkylsilanes and maleic or fumaric diesters, as described for example in EP 0 403 921.

Particularly suitable aminosilanes are the aminosilanes selected from the group comprising 3-aminopropyltrimethoxysilane, 3-aminopropyldimethoxymethylsilane, 3-amino-2-methylpropyltrimethoxysilane, 4-aminobutyltrimethoxysilane, 4-aminobutyldimethoxymethylsilane, 4-amino-3-methylbutyltrimethoxysilane, 4-amino-3,3-dimethylbutyltrimethoxysilane, 4-amino-3,3-dimethylbutyldimethoxymethylsilane, 2-aminoethyltrimethoxysilane, 2-aminoethyldimethoxymethylsilane, aminomethyltrimethoxysilane, aminomethyldimethoxymethylsilane, aminomethylmethoxydimethylsilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyldimethoxymethylsilane, 7-amino-4-oxaheptyldimethoxymethylsilane, and also their analogs with ethoxy or isopropoxy groups instead of the methoxy groups. Preference is given to 3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane.

Particularly suitable mercaptosilanes are the mercaptosilanes selected from the group comprising 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyldimethylmethoxysilane, and their analogs with ethoxy or isopropoxy groups instead of the methoxy groups. Preference is given to 3-mercaptopropyltrimethoxysilane and 3-mercaptopropyltriethoxysilane.

Hydroxy-epoxides can be prepared from an incomplete reaction of polyols with epichlorohydrin. They are also always present as by-products in the typically obtainable glycidyl ethers of polyols, and can be isolated by typical separating operations. Examples of such hydroxy-epoxides are trimethylolpropane diglycidyl ether (present as a mixture in trimethylolpropane triglycidyl ether), glycerol diglycidyl ether (present as a mixture in glycerol triglycidyl ether), and pentaerythritol triglycidyl ether (present as a mixture in pentaerythritol tetraglycidyl ether). Preference is given to using trimethylolpropane diglycidyl ether, which occurs in a relatively high proportion in typically prepared trimethylolpropane triglycidyl ether. It is, however, also possible to

use other, similar hydroxy-epoxides, especially glycidol, 3-glycidyloxybenzyl alcohol or hydroxymethylcyclohexene oxide. Of further preference is the β -hydroxy ether of the formula (III) present at about 15% in commercially customary liquid epoxy resins prepared from bisphenol A ($R = CH_3$) and
5 epichlorohydrin, and also the corresponding β -hydroxy ethers which are formed when bisphenol F ($R = H$) or the mixture of bisphenol A and bisphenol F is reacted with epichlorohydrin.



10 The compound **A** can also be obtained by a reaction of a polymer **A3-1** containing at least two isocyanate-reactive groups with at least one compound **AY**. The compound **AY** here contains an NCO group and also one or more alkoxy silane group. The polymer **A3-1** here may for example be a polyol, a polymercaptane or a polyamine. Also suitable for this purpose of course are
15 polymers which at the same time contain two or more different NCO-reactive groups. Particularly suitable polyols in this context include the polyols already described for the preparation of the polyurethane prepolymers **A3**. Particularly suitable polymercaptanes include mercapto-terminated polyalkylenes and Thiocols.

20 A further possibility for compounds **A3-1** are products from the reaction of polyols, polymercaptanes, polyols with polyisocyanates, specifically with a deficit amount of isocyanate. The deficit amount of isocyanates used is tailored in this case to the functionality of the polyisocyanate, polyol, polyamine or polymercaptane and also its molecular weight, so as to produce compounds
25 **A3-1** with not too high a viscosity. A further possibility is to prepare **A3-1** as adducts or chain extensions of a polyurethane prepolymer **A3** with diamines, diols or dimercaptanes in a stoichiometric excess.

The compound **AY** is an isocyanatosilane, in particular an isocyanatosilane selected from the group (3-isocyanatopropyl)trimethoxysilane

(isocyanatomethyl)methyldimethoxysilane, (isocyanatomethyl)trimethoxysilane, and their analogs with ethoxy or isopropoxy groups instead of the methoxy groups.

- 5 The composition of the invention further comprises at least one polymeric thixotropic agent **B**. This thixotropic agent may be obtained on the one hand by a homopolymerization reaction of a (meth)acrylate **B1** which contains three or more (meth)acrylate groups. The thixotropic agent may be obtained on the other hand by a copolymerization reaction of a (meth)acrylate
- 10 **B1** with at least one further (meth)acrylate, specifically such that the (meth)acrylate mixture possesses an average (meth)acrylate functionality \bar{f} of 2.5 to 4.5.

- The fraction of the polymeric thixotropic agent **B** is preferably between 0.1 and 10% by weight, in particular between 0.5% and 5% by weight, based
- 15 on the weight of the composition.

- A thixotropic agent **B** here must not contain any substantial fractions of functional groups which react with an NCO, epoxide or alkoxysilane group, since otherwise the composition lacks storage stability. Of course it is preferred that this fraction is zero or substantially zero. (Meth)acrylates **B1** having three
- 20 or more (meth)acrylate groups can be obtained from an esterification of triols and higher polyols. All (meth)acrylates used may be compounds of low or high molecular mass. Preference is given to using (meth)acrylates having a (meth)acrylate equivalent weight of 85 to 400 g/eq, in particular 85-150 g/eq, preferably 95-125 g/eq, corresponding to the molecular weight divided by the
- 25 number of (meth)acrylate groups per molecule. The (meth)acrylate **B1** preferably contains only (meth)acrylate groups as functional groups, and is preferably selected from the group comprising glycerol tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, pentaerythritol
- 30 tetra(meth)acrylate, glucose penta(meth)acrylate, sorbitol hexa(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and their ethoxylated or propoxylated analogs.

Particularly suitable are (meth)acrylates having three, four or five (meth)acrylate groups per molecule. Trifunctional (meth)acrylates are particularly preferred.

If the (meth)acrylate **B1** is copolymerized with a further monomer
5 (meth)acrylate, the (meth)acrylate mixture preferably has an average (meth)acrylate functionality \bar{f} of 2.5 to 3.5, with particular preference between 2.8 and 3.2.

Particularly preferred are monofunctional or difunctional (meth)acrylates, which can be copolymerized with tetrafunctional,
10 pentafunctional or hexafunctional (meth)acrylates.

Particularly suitable monofunctional (meth)acrylates are the monomers selected from the group comprising methyl (meth)acrylate, isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, 2-ethylhexyl (meth)acrylate and isobutyl (meth)acrylate.

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Particularly suitable difunctional (meth)acrylates are the (meth)acrylates selected from the group comprising C₂-C₈-alkylene di(meth)-acrylate, especially hexane di(meth)acrylate, ethylene glycol (meth)acrylate, diethylene glycol (meth)acrylate, triethylene glycol (meth)acrylate, tetraethylene
20 glycol (meth)acrylate, and also epoxy di(meth)acrylates.

By epoxy di(meth)acrylates are meant not only the reaction products of bisphenol A diglycidyl ethers with (meth)acrylic acid, but also esters of bisphenol A or alkoxyated bisphenol A with (meth)acrylic acid, especially with a molecular weight between 450 and 1000 g/mol.

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Preference is given above all to those (meth)acrylates which have no inherent odor or only a slight inherent odor. This is particularly important for interior applications, where such an inherent odor is disruptive.

The polymerization of the (meth)acrylates is accomplished by means of
30 free radicals. These free radicals may be generated in a way which is known to the skilled worker, in particular by means of light or heat, from a free-radical donor. The free radicals are preferably generated from organic peroxides.

Organic peroxides used advantageously are those having a decomposition temperature $T_{1/2}$ (1h) of between 100°C and 50°C, in particular between 70 and 95°C. The stated decomposition temperature is known to the skilled worker under the specialist English term "1 h half-life temperature". Organic peroxides
5 which have proven particularly preferred are those which are a peroxide of a fatty acid, especially dilauroyl peroxide.

On the basis of the free-radical donor used in the polymerization, the composition of the invention typically contains at least traces of the organic free-radical donor used for the free-radical polymerization of the
10 (meth)acrylates, or its derivative reaction products.

The composition may be one-component or two-component. In the case of the two-component composition the curing of the first component, which comprises the at least one compound **A** and at least one polymeric
15 thixotropic agent **B**, is cured by a second component, known as the hardener component. The second component comprises a compound **H** which reacts with the compound **A** or triggers a self-crosslinking. Typical examples of these compounds **H** are, for example, primary polyamines, polymercaptanes, polyols or water.

20 In the case of the one-component composition it cures by virtue of the fact that the compound **A** cures through the influence of heat or atmospheric moisture. If heat curing takes place, the composition may include a blocked or heat-reacting hardener **H'** which undergoes substantially no reaction with the compound **A** at room temperature but at an elevated temperature, typically at a
25 temperature of more than 80°C, undergoes deblocking and releases a compound **H** or reacts itself. Examples of a blocked or heat-reacting hardener **H'** are dicyandiamide or carboxylic anhydrides for a compound **A** having epoxy groups, or an acid-blocked amine for a compound **A** having epoxy groups or isocyanate groups.

30 Preferably the composition is one-component. If the compound **A** contains alkoxysilane and/or isocyanate groups, the composition is preferably

one-component and moisture-curing, curing in particular with moisture originating from the air.

In addition to the at least one compound **A** and the at least one
5 polymeric thixotropic agent **B**, the composition of the invention may further comprise at least one constituent known to the skilled worker for polyurethanes. silanes or epoxides, such as fillers, plasticizers, solvents, adhesion promoters, thixotropic agents, stabilizers, especially UV or heat stabilizers, or catalysts.

10 In the case of the two-component compositions the aforementioned constituents may in each case be present in both components or only in one component.

As a filler, carbon black is particularly preferred. The fraction of the filler, relative to the total composition, is typically between 25% and 50% by
15 weight, in particular between 25% and 45% by weight, preferably between 30% and 40% by weight, based on the weight of the composition, especially for an adhesive or sealant.

In one embodiment of the present invention the composition contains no carbon black. It is therefore possible to produce light-colored compositions
20 and also colored compositions, especially white compositions, more particularly white polyurethane adhesives.

Particularly suitable adhesion promoters are trialkoxysilanes, especially trimethoxysilanes. These are preferably methacryloyloxy-, epoxy-, mercapato- or vinyl-silanes, especially methacryloyloxypropyltrimethoxysilane, 3-glycidyloxy-
25 propyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane or vinyltriethoxysilane. With further preference the adhesion promoter may comprise adducts between trialkoxysilanes which carry primary amino groups, especially 3-aminopropyltrimethoxysilane or 3-(2-aminoethylamino)propyltrimethoxy-
30 trimethoxysilane, 3-mercaptopropyltrimethoxysilane.

Particularly suitable plasticizers are phthalates or adipates, especially dialkyl phthalates, preferably diisodecyl phthalate, or dialkyl adipates, preferably dioctyl adipate.

5 In one embodiment of the present invention the composition has a solvent content of less than 5% by weight, in particular of less than 1% by weight, and a plasticizer content of less than 5% by weight, in particular of less than 1% by weight. With preference the composition is free of solvent, in particular free of solvent and free of plasticizer.

10 It is particularly preferred for the polymeric thixotropic agent **B** to be a constituent of a plasticizer-free composition.

The composition contains advantageously less than 1% by weight, preferably less than 0.1% by weight, in particular 0% by weight, of substances considered to be VOCs (Volatile Organic Compound).

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There are two preferred ways of preparing the composition. In a first version the compound **A** is prepared to start with, in the absence of moisture in the case of moisture-reactive compounds **A**. For this purpose the polymeric thixotropic agent **B**, which is polymerized in a separate production process, initiated by free-radical donors, from the (meth)acrylate or the relevant (meth)acrylates, and where appropriate has been prepared in further worked-up form, is added, advantageously with vigorous stirring. Prior to the addition, this thixotropic agent is in the form in particular of a powder, preferably a spray-dried powder, or in the form of a solution or dispersion, in particular in an adipate or phthalate plasticizer.

25

The thixotropic agent is advantageously added at a temperature of the kind typically chosen for the preparation of the compound **A**, in particular at 50-80°C.

Subsequently, if present, the further constituents are typically mixed in. In particular the plasticizers, solvents, catalysts or stabilizers, where present, may have been admixed at least in part to the compound **A** or to its starting product even prior to the addition of thixotropic agent.

30

In a second version the thixotropic agent **B** is polymerized in situ. This version of the preparation takes place advantageously as follows. In a first step the compound **A** is prepared, in the absence of moisture in the case of moisture-reactive compounds **A**. It may be of advantage that the compound **A** even at this early point contains solvent or plasticizer. Subsequently the (meth)acrylate or the (meth)acrylates, either together or in succession, are added to the compound **A**. Subsequently, typically, a polymerization catalyst, where used, is added, and then a free-radical donor. In certain circumstances, however, it may be of advantage for any polymerization catalyst and the free-radical donor to have been already added prior to the addition of the (meth)acrylate to the compound **A**. In situ homopolymerization or copolymerization of the thixotropic agent **B** takes place with stirring at a temperature of typically 80-95°C. Subsequently, typically, the further constituents, if present, are mixed in.

15

If the compound **A** is a moisture-reactive compound, it is necessary to ensure in each step during the preparation of the composition that, on the one hand, not only the reactants but also the constituents contain as little water as possible and, on the other hand, that any preparation and processing steps take place with strict exclusion of moisture, and in particular under inert gas.

20

Production is followed by dispensing into packaging appropriate for storage, transport, and application. The packaging in question comprises, in particular, cartridges, pails, hobbocks, pouches or Unipack casings. In the choice of packaging materials it is necessary to ensure that the pack is impervious and offers sufficient moisture protection so that the shelf life of at least 6 months, in particular at least 9 months, is ensured without hardening or substantial thickening.

25

In the case of application as a two-component composition, the first and second components are intimately mixed with one another, using a mixing gun or a mixer, for example, and the mixture is immediately contacted at least

30

partly with the surface of any desired substrate. As a result of a reaction, in particular an addition reaction, the reactive composition **A** reacts with the compound **H** and an article is produced which is in frictional contact with the cured composition.

5

In the case of application as a one-component composition the isocyanate groups and/or alkoxysilane groups of the compound **A** come into contact with moisture, whereupon they react with water and crosslink. This cures the composition. Alternatively the water needed for curing can come from
10 the air (atmospheric humidity), or the composition can be contacted with a water-containing component, by being spread-coated, for example, with a smoothing agent, for example, by being sprayed, or by means of immersion processes, or else the composition can have a water-containing component added to it, in the form for example of a hydrous paste, which is mixed in via a
15 static mixer, for example.

The composition described can be used as an adhesive, sealant, coating or covering. Its preferred use is as an adhesive or sealant. In the sealant utility, joints in the construction of built structures and industrial products, in particular, are filled and sealed with the composition.

20 In the adhesive utility, the composition is employed in particular for the bonding of diverse substrates, such as for bonding components in the production of automobiles, rail vehicles, ships or other industrial products, and also as a coating or covering for diverse articles and/or variable substrates. Preferred coatings are protective paints, seals, protective coatings, and
25 primers. Among the coverings, floor coverings in particular may be mentioned as preferred. Such coverings are produced by, typically, pouring a composition onto the substrate and leveling it, where it cures to form a floor covering. Floor coverings of this kind are used, for example, for offices, living areas, hospitals, schools, warehouses, multistory carparks and other private or industrial
30 applications.

Where the compound **A** is a compound which carries epoxide groups and is cured by means of a second, hardener component, in particular with

polyamines, this composition can be employed to great advantage in the construction of built structures, such as buildings, bridges, and tunnels. For these purposes it is necessary for the adhesives employed to exhibit very good adhesion to concrete, mineral substrates, and steel and also to have great
5 inherent strengths.

The composition is at least partly contacted with the surface of any desired substrate. Preference is given to uniform contacting in the form of a sealant or adhesive, a coating or a covering, in the regions which for use
10 require a connection in the form of an adhesive bond or seal, or else whose substrate is to be covered. It may well be necessary for the substrate or article to be contacted to have to undergo physical and/or chemical pretreatment prior to contacting, such as by sanding, sandblasting, brushing or the like, for example, or by treatment with cleaning products, solvents, adhesion
15 promoters, adhesion-promoter solutions or primers, or the application of a tie coat or a sealer. Contacting is followed in the case of moisture-reactive compositions, as already mentioned, by curing under the influence of water.

Finally an article is produced which is in frictional contact with the cured composition.

20

The compositions of the invention are thixotropic. This is manifested in qualities which include that of an improved flow resistance. Moreover, the compositions of the invention preferably have a thixotropic index (TI) of more than 6, in particular of more than 10, preferably of more than 20, which is a
25 product of the ratio of the viscosities at a shear rate of 1s^{-1} and at a shear rate of 100s^{-1} , measured at a temperature of 20°C :

$$\text{TI} = \frac{\eta(1\text{s}^{-1})}{\eta(100\text{s}^{-1})} \geq 1$$

30 It has further emerged that these compositions are also distinguished by a greatly reduced gloss. Too high a gloss can be disadvantageous for

adhesives and sealants, since those with a high gloss value can reflect light and therefore tend to be more conspicuous. Low degrees of gloss are preferred, therefore, primarily on esthetic grounds. It has been possible to demonstrate that the compositions of the invention exhibit a greatly reduced
5 gloss as compared with their counterparts without thixotropic agent. Accordingly the polymeric thixotropic agent **B** can also be used as a polymeric matting agent for adhesives, sealants, and coverings.

It has additionally been found that the polymeric thixotropic agent **B**
10 contains small particles which are slightly different depending on operating parameter. Particle sizes which have been found particularly suitable are those of less than 5 micrometers, particularly those of less than 0.5 micrometer. Excessively large particles lead to particle settlement and hence to storage stability problems, and also to a deterioration in the thixotroping properties.

15

Examples

Production of composition comprising thixotropic agent B

1.) Composition containing isocyanate groups

Preparation of a polyurethane prepolymer *Prep1*

- 5 2155 g of Acclaim[®] 4200 N polyol (Bayer), 4310 g of Caradol[®] MD34-02 polyol (Shell) and 1035 g of methylenediphenyl 4,4'-diisocyanate (MDI; Desmodur[®] 44 MC L, Bayer) were reacted by a known method at 80°C to give an NCO-terminated prepolymer. The reaction product had a titrimetrically determined free isocyanate group content of 2.36% by weight. *Prep1* is an example of a
10 compound **A3**.

- To prepare a 5% by weight composition, 470 g of *Prep1* were admixed with 25 g of a (meth)acrylate **B** or a mixture of a (meth)acrylate **B** with a further (meth)acrylate, and the mixture was blanketed with nitrogen and heated at
15 90°C with stirring. It was admixed with a further mixture, consisting of 1.5 g of dilauroyl peroxide and 3.5 g of diisodecyl phthalate. The combined mixture was stirred while the formation of gel was awaited, which occurred after about 10 minutes. Subsequently the mixture was stirred further at 90°C for about 30 minutes more and then cooled to room temperature.

20

To prepare a 10% by weight composition, an analogous procedure was followed using 445 g of *Prep1* and 50 g of a (meth)acrylate **B** or mixture of a (meth)acrylate **B** with a further (meth)acrylate.

25 Suitability of the thixotropic agent

- To assess its suitability as a thixotropic agent, the respective composition was dispensed into an aluminum cartridge and applied as a triangular bead to a horizontal surface; after 7 days the bead was cut open and the deviation from the triangular shape was assessed in accordance with the following
30 assessment code with regard to % by weight of **B**, based on the weight of the composition:

- 1 no substantial deviation at 5% by weight

- 2 mild deviation at 5% by weight, no deviation at 10% by weight
 3 strong deviation at 5% by weight, slight deviation at 10% by weight
 4 very strong deviation at 10% by weight

The suitability of the compositions **B** as thixotropic agents was the thixotropic

- 5 agents prepared as follows:

Designation	Monomer	\bar{f}	Suitability
1	Dipentaerythritol pentaacrylate (DiPEPA)	5	2
2	Ditrimethylolpropane tetraacrylate (DiTMPTTA)	4	2
3	Pentaerythritol tetraacrylate (PETA-4)	4	1
4	Trimethylolpropane trimethacrylate (TMPTMA)	3	1
5	Trimethylolpropane triacrylate (TMPTA)	3	1
6	Pentaerythritol triacrylate (PETA-3)	3	1
7	Tris(2-hydroxyethyl)isocyanurate triacrylate	3	2
8	Isobutyl methacrylate/PETA-4 (3 mol/7 mol)	3	1
9	Methyl methacrylate/PETA-4 (3 mol/7 mol)	3	1
10	Isobutyl methacrylate/PETA-4 (3 mol/4 mol)	2.7	2
11	Methyl methacrylate/PETA-4 (3 mol/4 mol)	2.7	2
Ref.1	Hexanediol diacrylate	2	3
Ref.2	Methyl methacrylate/PETA-4 (9 mol/1 mol)	1.3	4
Ref.3	Methyl methacrylate/TMPTA (9 mol/1 mol)	1.2	4
Ref.4	Isobornyl methacrylate (IBOMA)	1	4
Ref.5	Isobornyl acrylate (IBOA)	1	4
Ref.6	Methyl methacrylate (MMA)	1	4
Ref.7	2-Ethylhexyl acrylate (EHA)	1	4
Ref.8	Isobutyl methacrylate	1	4
Ref.8	1,6-Hexanediol dimethacrylate (HDDMA)	2	3
Ref.9	1,6-Hexanediol diacrylate (HDDA)	2	3

Table 1 Suitability as thixotropic agents.

Epoxy resin-based composition

100 g of trimethylolpropane trimethacrylate (TMPTMA) were dissolved with stirring at 90°C in 1000 g of liquid bisphenol A diglycidyl ether resin (BADGE) (Araldite ® GY 250). The reaction vessel was evacuated three times
5 and flooded with nitrogen. The reaction was carried out under nitrogen. After about 30 minutes, 3 g of dilauroyl peroxide were added and the mixture was stirred vigorously. This produced a glassy mass of high viscosity. The epoxy content of this paste, referred to below as *EP-Paste1*, was 4.6 eq/kg. This *EP-Paste1* had a **B** content of 9.1% by weight.

10

Production of adhesives

1. Polyurethane adhesives

One-component moisture-curing polyurethane adhesives of the composition indicated in Table 2 were produced. For a 5 kg batch in
15 accordance with the quantities of Table 2, first of all the (meth)acrylate was added to *Prep1* and plasticizer, and the mixture was blanketed with nitrogen and heated at 90°C with stirring. At 90°C the peroxide was added. The mixture was subsequently stirred for 10 minutes more and then cooled to 50°C. At this
20 point the drying agent and also carbon black and kaolin were mixed in, and mixing was carried out under reduced pressure for 15 minutes. This gave a homogeneous black paste. Finally the catalyst was added, a further 10 minutes of stirring were carried out, and the mixture was dispensed into aluminum cartridges.

Designation	<i>KP-Ref.1</i>	<i>KP1</i>	<i>KP2</i>	<i>KP3</i>	<i>KP4</i>	<i>KP5</i>	<i>KP6</i>
Prepolymer (<i>Prep1</i>)	45.0	45.0	45.0	45.0	45.0	45.0	45.0
Diisodecyl phthalate	24.7	24.7	24.7	24.7	24.7	24.7	24.7
TMPTMA	0.00	1.75	2.25	3.00	3.50	4.00	5.25
Dilauroyl peroxide	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Drying agent	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Carbon black	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Kaolin	14.6	12.9	12.4	11.6	11.1	10.6	9.35
Catalyst	0.10	0.10	0.10	0.10	0.10	0.10	0.10

Table 2. Polyurethane adhesive compositions (Amounts in% by weight)

2. Epoxy resin adhesives

2.1. 1-Component thermosetting epoxy resin adhesives

- 5 EP-Paste1 was weighed out together with bisphenol A diglycidyl ether, the epoxy reactive diluent, dicyandiamide, and the fillers into a sheet metal canister and homogenized at 50°C under reduced pressure for 1 h.
- Subsequently a sheet of adhesive was produced from the adhesive and cured at 180°C for 30 minutes. Dumbbell specimens were produced by punching and
- 10 then tested for tensile strength, breaking extension, and elasticity modulus (dumbbells, length: 75 mm, width: 4 mm, thickness: 2 mm; testing speed: 2 mm/min (DIN 53 504)) (see Table7).

Designation	<i>KE-Ref.1</i>	<i>KE1</i>
BADGE	60.0	10.0
<i>EP-Paste 1</i>	-	55.0
Polypropylene glycol diglycidyl ether	10.0	10.0
Dicyandiamide	5.0	5.0
Wollastonite	12.0	12.0
Chalk	13.0	13.0
<i>Total:</i>	<i>100.0</i>	<i>105.0</i>
Overall concentration of B [%]	0	4.7

Table 3. Compositions of 1-comp. epoxy resin adhesives (all amounts in parts by weight)

2.2 2-Component epoxy resin adhesives

EP-Paste1 was weighed out together with bisphenol A diglycidyl ether, the
 5 reactive diluent and the fillers into a sheet metal canister and homogenized at
 40°C under reduced pressure for 1 h.

Subsequently a mixture of amines and accelerator was added to the canister
 and stirred under reduced pressure for 5 minutes more. The adhesive was
 transferred to a cartridge and immediately discharged into a sample casting
 10 mold.

The samples were stored under standard conditions for 7 days, then removed
 from the mold and subjected to testing in a 3-point flexural test: dumbbells,
 length: 150 mm, width: 10 mm, thickness: 10 mm; testing speed: 2 mm/min (in
 analogy to ISO 178) (see Table 8).

Designation	KE-Ref.2	KE2	KE-Ref.3	KE3
First component (resin)				
BADGE	60.0	10.0	68.5	-
EP-Paste1	-	55.0	-	75.0
Polypropylene glycol diglycidyl ether	10.0	10.0	-	-
Wollastonite	20.0	20.0	10.0	10.0
Chalk	20.0	20.0	18.0	18.0
Second comoponent (hardener)				
Isophoronediamine	13.0	13.0	13.4	13.4
1,3-Xylylenediamine	15.0	15.0	15.6	15.6
2,4,6 Tri(dimethylaminomethyl)phenol	5.0	5.0	5.2	5.2
Total:	143.0	148.0	130.70	137.2
Overall concentration of B [%]	0	3.3	0	4.9

Table 4. Compositions of 2-comp. epoxy resin adhesives (all amounts in parts by weight)

3. Alkoxysilane adhesives

5 Preparation of *Prep2*:

Prep2 is the reaction product of an isocyanate-terminated prepolymer (prepared by conventional preparation process from Acclaim®12200 (Bayer) and IPDI, NCO/OH ratio of 2) with the aminosilane from Example 5 of US 5,364,955. This reaction takes place conventionally. *Prep2* has a

10 titrimetrically determined free isocyanate group content of 0.00% by weight.

Production of *KS1*:

In a commercially customary 1 kg mixer, 270 g (100 parts) of the alkoxysilane-functional polyurethane prepolymer *Prep2* were mixed with 100 g

15 (37 parts) of DIDP plasticizer for 5 minutes. Added to this mixture were 20 g (7 parts) of trimethylolpropane trimethacrylate (TMPTMA, Fluka Chemie) and 2.4 g (0.9 part) of dilauroyl peroxide (Fluka Chemie), and the mixture was

heated at 90°C. It was then stirred at 90°C under reduced pressure for 30 minutes until a highly viscous, flow-resistant mass had formed. Then 54 g (20 parts) of titanium dioxide and 325 g (120 parts) of coated chalk were mixed in at 60°C for 15 minutes. Subsequently 8 g (3 parts) of diaminosilane
5 (Silquest® A-1120), 2.7 g (1 part) of UV stabilizer (Tinuvin 5060, Ciba Specialities) and 5.4 g (2.1 parts) of vinylsilane (Silquest® A-171) were added and stirred in without heating but under reduced pressure for 10 minutes. Finally a further 1.18 g (0.5 part) of dibutyltin dilaurate (DBTL) and 10 g (4 parts) of DIDP plasticizer were added and mixed in under reduced pressure
10 for 10 minutes.

A similar procedure was adopted for the examples indicated in Table 5. In the examples **KMS1** and **KMS-Ref.1**, instead of the alkoxysilane-functional polyurethane prepolymer *Prep2* (as an example of a compound **A2-1**), a
15 commercial MS polymer (MS-S303H, available from Kaneka Corp.) was employed (as an example of a compound **A2-2**). In the case of the reference adhesives **KS-Ref.1** and **KMS-Ref.1**, however, no TMPTMA or peroxide was used, and hence the step of heating to 90°C was also omitted.

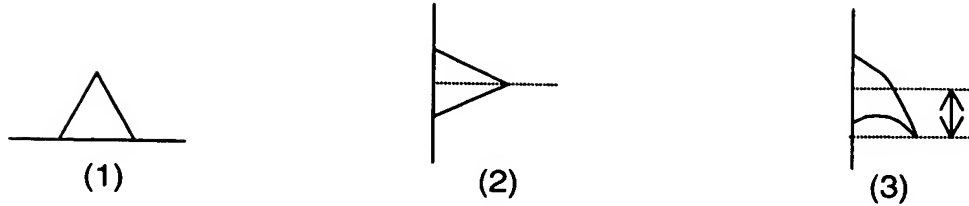
Designation	KS1	KS2	KS-Ref.1	KMS1	KMS-Ref.1
Prep2	100	100	100	-	-
MS-S303H (Kaneka Corp.)	-	-	-	100	100
Diisodecyl phthalate	37	37	37	39	46
TMPTMA	7	4	0	7	0
Dilauroyl peroxide	0.9	0.9	0	0.9	0
Titanium dioxide	20	20	20	20	20
Coated chalk	120	120	120	120	120
Aminosilane (Silquest A-1120)	3	3	3	3	3
Tinuvin 5060	1	1	1	1	1
Vinylsilane (Silquest A-171)	2	2	2	2	2
Dibutyltin dilaurate	0.44	0.44	0.48	1.82	1.82
Diisodecyl phthalate	4	4	19	6	6
<i>Total</i>	<i>295.34</i>	<i>292.34</i>	<i>302.48</i>	<i>300.72</i>	<i>299.82</i>
Overall concentration of B [%]	2.4	1.4	0	2.3	0

Table 5. Compositions of alkoxysilane adhesives (all amounts in parts by weight).

Results

The following properties were determined on these adhesives, and are summarized in Tables 6 to 9:

- Sagging: A triangular bead (height 22 mm, base 8 mm) was applied to a glass plate (1). Subsequently the plate was immediately set up vertically (2) and cured at room temperature and 50% relative humidity. An assessment was made of the flow resistance, by measuring the sagging of the adhesive (3). Depicted diagrammatically:



- Viscosity: The viscosity was determined with a viscometer (Rheomat) (5 s^{-1} , 20°C , plate $\varnothing = 25\text{mm}$, slot thickness 1 mm)
- 5
- Adhesion to glass: The glass surface (floatglass, available commercially from Rocholl, Schönbrunn, Germany) was pretreated with Sika® activator (available commercially from Sika Schweiz AG). After a flash-off time of 30 minutes the adhesive was applied and was cured for 7 days at room temperature and 50% relative humidity. Subsequently the sample was
- 10
- stored in water at room temperature for 7 days, then stored in a drying cabinet at 80°C for 1 day, and finally for 7 days under hot humid conditions (70°C and 100% relative humidity). After each storage period the adhesion was tested by means of the bead test. In this test an
- 15
- incision is made at the end just above the adhesive area. The incized end of the bead is held with round-ended tweezers and pulled from the substrate. This is done by carefully rolling the bead onto the tip of the tweezers, and placing a cut down to the bare substrate perpendicular to the direction in which the bead is pulled. The speed at which the bead is removed by pulling should be selected such that it is necessary to make
- 20
- a cut about every 3 seconds. The test distance must be at least 8 cm. An assessment is made, after the bead has been removed by pulling, of the adhesive which remains on the substrate (cohesive fracture). The attachment properties are evaluated by estimating the cohesive fraction of the attachment area:

25

- 1 = > 95% cohesive fracture
- 2 = 75 - 95% cohesive fracture
- 3 = 25 - 75% cohesive fracture

4 = < 25% cohesive fracture

5 = adhesive fracture

- 5 - Tensile shear strength: to DIN EN 1465 (20 mm/min)
- Tensile strength: to DIN 53504 (200 mm/min)
- Breaking extension: to DIN 53504 (200 mm/min)
- 10 - Elasticity modulus: to DIN 53504 (200 mm/min)
- Tear propagation resistance DIN 53515 (500mm/min)
- 15 - Thixotropic Index (TI): The ratio of the viscosities at a shear rate of 1 s^{-1} and 100 s^{-1} , measured at a temperature of 20°C

$$\text{TI} = \frac{\eta(1\text{s}^{-1})}{\eta(100\text{s}^{-1})} \geq 1$$

- 20 -Extrusion force (EF): For the determination of the extrusion force a cartridge filled with adhesive was conditioned at 23°C for 12 hours and then opened and fitted with a screw-on nozzle of 5 mm. And, using a Zwick 1120 extrusion apparatus, a measurement was made of the force required to extrude the adhesive with a speed of 60 mm/min. The figure reported is an average value after extrusion of 85 ml.

25

Designation	KP-Ref.1	KP1	KP2	KP3	KP4	KP5	KP6
Amount of B [%]	0.00	1.75	2.25	3.00	3.50	4.00	5.25
Sagging [mm]	32	14	9	2	0.5	0	0
Viscosity [Pas]	256	1200	1750	2360	3150	3770	6180
Adhesion to glass							
7d/RT	1	1	1	1	1	1	1
7d/water	1	1	1	1	1	1	1
1d/80°C	1	1	1	1	1	1	1
7d/hot-humid	1	1	1	1	1	1	1
Tensile shear strength [MPa]	4.8	4.5	4.7	5.7	5.8	5.7	6.5
Tensile strength [MPa]	7.4	7.9	8.2	8.6	8.7	9.4	9.7
Breaking extension [%]	370	340	330	340	330	340	320
Elasticity modulus (0.5-1.0%)[MPa]	2.4	3.1	3.5	3.8	4.1	4.3	4.5
Thixotropic Index (TI):	5.1	15.4	22.7	23.5	25.5	31.3	N/A ^x
Extrusion force [N]	29	463	500	694	827	965	1515

Table 6. Properties of the polyurethane adhesives.

^x Viscosity at a shear rate of 1 s⁻¹ can no longer be measured

Designation	KE-Ref.1	KE1
Overall concentration of B [%]	0	4.7
Sagging after 1 week under standard conditions [mm]	> 50	0
Sagging after curing (30' 180°C) [mm]	> 50	10
Tensile strength [MPa]	62.0	71.0
Breaking extension [%]	2.5	4.5
Elasticity modulus (0.5-1.0%) [MPa]	3200	3175

Table 7. Properties of the 1-component epoxy resin adhesives.

Designation	<i>KE-Ref.2</i>	<i>KE2</i>	<i>KE-Ref.3</i>	<i>KE3</i>
Overall concentration of B [%]	0	3.3	0	4.9
Sagging after 1 week standard conditions [mm]	> 50	2	> 50	0
Maximum force 3-point flexing [MPa]	25.5	24.1	11.2	11.1
Initial modulus 3-point flexing [MPa]	4780	4160	3710	3770

Table 8. Properties of the 2-component epoxy resin adhesives.

Designation	<i>KS1</i>	<i>KS2</i>	<i>KS-Ref.1</i>	<i>KMS1</i>	<i>KMS-Ref.1</i>
Amount of B [%]	2.4	1.4	0	2.3	0
Flow resistance	good	good	poor	good	poor
Sagging [mm]	3	5	>50	3	>50
Tensile strength [MPa]	2.9	2.4	2.2	2.5	2.0
Breaking extension [%]	169	195	236	467	386
Tear propagation resistance [N/mm]	4.5	4.3	5.5	16.7	15.4
Elasticity modulus 0-5% [MPa]	4.8	3.8	2.0	2.0	2.0
Elasticity modulus 0-25% [MPa]	3.5	3.0	1.7	1.4	1.2
Elasticity modulus 0-50% [MPa]	3.0	2.5	1.4	1.2	1.0
Elasticity modulus 0-100% [MPa]	2.3	2.0	1.3	1.0	0.8
Shore A	60	55	46	20	37

Table 9. Properties of the alkoxysilane adhesives.

Tables 6 to 9 show that even small amounts of the polymeric
5 thixotropic agent **B** result in the compositions formulated therewith having flow resistance and being useful as adhesives. In particular it is apparent that the

addition of the polymeric thixotropic agent **B** does not lead to any impairment, or any substantial impairment, in the mechanical properties.

Suitability as matting agents

- 5 The gloss value was measured by means of light reflection on a layer 2 mm thick drawn down planarly onto a glass plate using a wood slot. After drying for 24 hours, a measurement was made of the gloss value as a triplicate determination using a gloss meter (Erichsen Pico Glossmaster 500-20°/60°) at a gloss angle of 60°.

10

Designation	<i>KP-Ref.1</i>	<i>KP1</i>	<i>KP2</i>	<i>KP3</i>	<i>KP4</i>	<i>KP5</i>	<i>KP6</i>
Amount of B [% by weight]	0.00	1.75	2.25	3.00	3.50	4.00	5.25
Gloss value (60°)	73.9	58.9	45.4	16.2	9.6	6.8	3.2

Table 10 Compound **B** as a matting agent.

It is evident from Table 10 that compound **B** acts as a matting agent. Even a small concentration of this substance results in a substantial loss of gloss by the composition.

15